

# Lecture 4. Composition and structure of the Earth's atmosphere. Basic properties of gases, aerosols, and clouds.

## Objectives:

1. Composition of the atmosphere: main physical and chemical properties of gases, aerosols, and clouds.
2. Structure of the atmosphere. Temperature lapse rate. Hydrostatic equation and the scale height. Global energy budget.

## Required reading:

L02: 3.1, 5.1

# 1. Composition of Atmosphere.

## Atmospheric gases.

**Table 4.1** Three most abundant gases in each planetary atmosphere (Yung and DeMore, 1999). *Mixing ratios are given in parentheses. All compositions refer to the surface or 1 bar for the giant planets.*

Jupiter	H <sub>2</sub> (0.93)	He (0.07)	CH <sub>4</sub> ( $3.0 \times 10^{-3}$ )
Saturn	H <sub>2</sub> (0.96)	He (0.03)	CH <sub>4</sub> ( $4.5 \times 10^{-3}$ )
Uranus	H <sub>2</sub> (0.82)	He (0.15)	CH <sub>4</sub> ( $1 - 2 \times 10^{-2}$ )
Neptune	H <sub>2</sub> (0.80)	He (0.19)	CH <sub>4</sub> ( $2.0 \times 10^{-3}$ )
Titan	N <sub>2</sub> (0.95-0.97)	CH <sub>4</sub> ( $3.0 \times 10^{-2}$ )	H <sub>2</sub> ( $2.0 \times 10^{-3}$ )
Triton	N <sub>2</sub> (0.99)	CH <sub>4</sub> ( $2.0 \times 10^{-2}$ )	CO (<0.01)
Pluto	N <sub>2</sub> (?)	CH <sub>4</sub> (?)	CO (?)
Io	SO <sub>2</sub> (0.98)	SO (0.05)	O (0.01)
Mars	CO <sub>2</sub> (0.95)	N <sub>2</sub> ( $2.7 \times 10^{-2}$ )	Ar ( $1.6 \times 10^{-2}$ )
Venus	CO <sub>2</sub> (0.96)	N <sub>2</sub> ( $3.5 \times 10^{-2}$ )	SO <sub>2</sub> ( $1.5 \times 10^{-4}$ )
Earth	N <sub>2</sub> (0.78)	O <sub>2</sub> (0.21)	Ar ( $9.3 \times 10^{-3}$ )

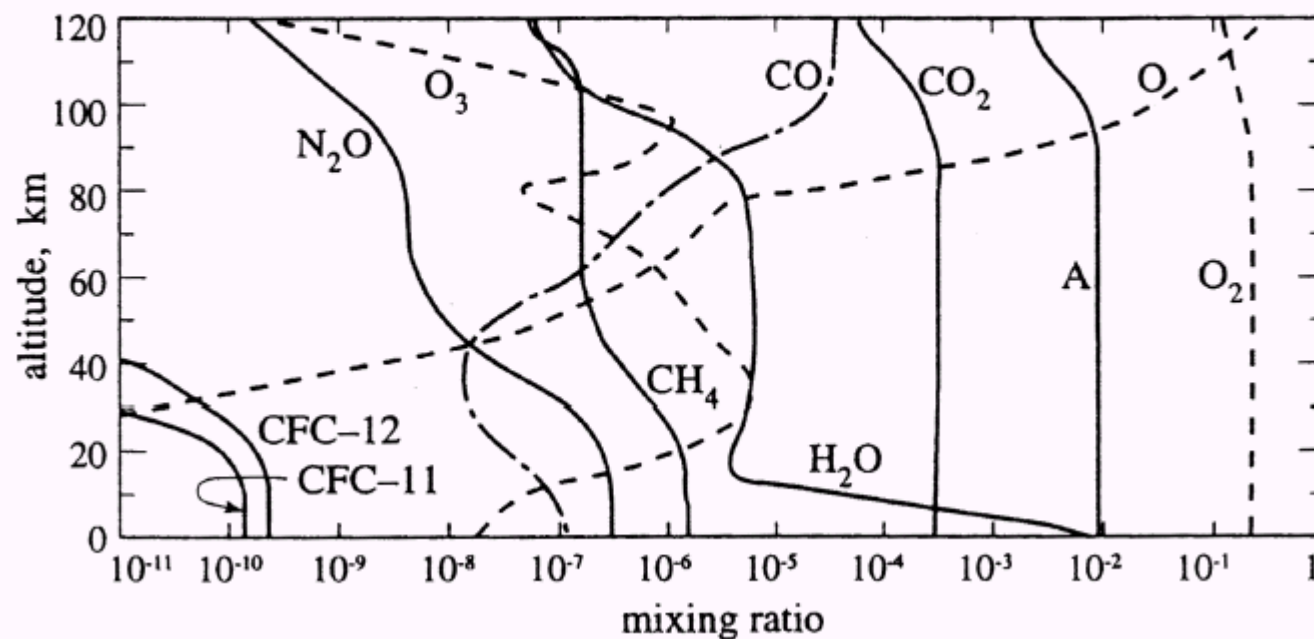
Table 4.2 The gaseous composition of the Earth's atmosphere

Gases	% by volume	Comments
<b>Constant gases</b>		
Nitrogen, N <sub>2</sub>	78.084%	Photochemical dissociation high in the ionosphere; mixed at lower levels
Oxygen, O <sub>2</sub>	20.948%	Photochemical dissociation above 95 km; mixed at lower levels
Argon, Ar	0.934%	Mixed up to 110 km
Neon, Ne	0.001818%	Mixed in most of the middle atmosphere
Helium, He	0.000524%	
Krypton, Kr	0.00011%	
Xenon, Xe	0.000009%	

### Variable gases

Water vapor, H <sub>2</sub> O	4.0% (maximum, in the tropics) 0.00001%(minimum, at the South Pole)	Highly variable; photodissociates above 80 km dissociation
Carbon dioxide, CO <sub>2</sub>	0.0365% (increasing ~0.4% per year)	Slightly variable; mixed up to 100 km; photodissociates above
Methane, CH <sub>4</sub>	~0.00018% (increases due to agriculture)	Mixed in troposphere; dissociates in mesosphere
Hydrogen, H <sub>2</sub>	~0.00006%	Variable photochemical product; decreases slightly with height in the middle atmosphere
Nitrous oxide, N <sub>2</sub> O	~0.00003%	Slightly variable at surface; dissociates in stratosphere and mesosphere
Carbon monoxide, CO	~0.000009%	Variable
Ozone, O <sub>3</sub>	~0.000001% - 0.0004%	Highly variable; photochemical origin
Fluorocarbon 12, CF <sub>2</sub> Cl <sub>2</sub>	~0.00000005%	Mixed in troposphere; dissociates in stratosphere

**Figure 4.1** Vertical profiles of mixing ratios of some gases in the atmosphere.



# Some important properties of atmospheric gases.

- *Obey the ideal gas laws:*

**Boyle's law:**  $V \sim 1/P$  (at constant  $T$  and the number of gas moles  $\mu$ )

**Charles's law:**  $V \sim T$  (at constant  $P$  and  $\mu$ )

**Avogadro's law:**  $V \sim \text{number of gas molecules}$  (at constant  $P$  and  $T$ )

**The equation of state:** says that the pressure exerted by a gas is proportional to its temperature and inversely proportional to its volume:

$$P V = \mu R T$$

where  $R$  is the universal gas constant. If pressure  $P$  is in atmospheres (atm), volume  $V$  in liters (L) and temperature  $T$  in degrees Kelvin (K), thus  $R$  has value

$$R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

*The distribution of velocities* of ideal gas molecules (e.g., atmospheric gases) is described by the Maxwell-Boltzmann velocity distribution law:

$$f(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp \left( -\frac{mv^2}{2k_B T} \right)$$

where  $v$  is velocity (m/s);  $m$  is mass of a gas molecule (kg),  $T$  is temperature (K), and  $k_B$  is Boltzmann's constant =  $1.38066 \times 10^{-23}$  (J/K).

**NOTE: Most probable velocity**  $v$  (the velocity possessed by the greatest number of gas particles):  $v = (2k_B T / m)^{1/2}$  and the **mean velocity** of a gas molecule is

$$v = (8k_B T / \pi m)^{1/2}$$

The amount of the gas may be expressed in several ways:

i) **Molecular number density = molecular number concentration = molecules per unit volume of air;**

ii) **Density = molecular mass concentration = mass of gas molecules per unit volume of air;**

iii) **Mixing ratios:**

**Volume mixing ratio** is the number of gas molecules in a given volume to the total number of all gases in that volume (when multiplied by  $10^6$ , in ppmv (parts per million by volume))

**Mass mixing ratio** is the mass of gas molecules in a given volume to the total mass of all gases in that volume (when multiplied by  $10^6$ , in ppmm (parts per million by mass))

**NOTE:** Commonly used mixing fraction: one part per million 1 **ppm** ( $1 \times 10^{-6}$ ); one part per billion 1 **ppb** ( $1 \times 10^{-9}$ ); one part per trillion 1 **ppt** ( $1 \times 10^{-12}$ ).

iv) **Mole fraction** is the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.

**NOTE:** mole fraction is equivalent to the volume fraction.



Ideal gas law is  $p = \rho T R_g$ ;  $p$  is pressure,  $T$  is temperature, and  $\rho$  is density.

Hydrostatic relation is  $dp/dz = -g\rho$ .

Dry adiabatic lapse rate is  $\Gamma_a = -dT/dz = g/c_p$ .

Exponential scale height is  $p \approx p_{sfc} \exp(-z/H)$  ( $H$  depends on  $T$ ).

**NOTE:** The equation of state can be written in several forms:

using molar concentration of a gas,  $c = \mu/v$ :  **$P = c T R$**

using number concentration of a gas,  $N = c N_A$ :  **$P = N T R/N_A$  or  $P = N T k_B$**

using mass concentration of a gas,  $q = c m_g$ :  **$P = q T R / m_g$**

# Basic properties of terrestrial planet atmospheres

	Earth	Mars	Venus
mean distance from Sun ( $\times 10^6$ km)	150	228	108
Eccentricity	0.017	0.093	0.007
Obliquity (tilt)	23.5	24	177
mean radius (km)	6371	3390	6052
length of solar day (days)	1	1	117
albedo	0.30	0.20	0.80
mean surface temperature (K)	288	215	730
mean surface pressure (bars)	1.01	$\sim 0.007$	92
surface gravity $g$ (m/s <sup>2</sup> )	9.8	3.7	8.9
pressure scale height $H$ (km)	8.5	10.5	15
dry adiabatic lapse rate (K/km)	9.8	4.5	10.5
mean lower atmos. lapse rate (K/km)	6.5	3	8
specific heat $c_p$ (kJ kg <sup>-1</sup> K <sup>-1</sup> )	1.004	0.83	0.85
gas law constant $R_g$ (J kg <sup>-1</sup> K <sup>-1</sup> )	287	189	189
mean molecular weight (g/mole)	29.0	43.2	43.5
cloud cover	60%	10%	100%

# The structure of the molecule

The structure of molecules is important for an understanding of their energy forms:

- ✓ Linear molecules ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ;  $\text{C}_2\text{H}_2$ , all diatomic molecules):
  - ✓ Symmetric top molecules ( $\text{NH}_3$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CF}_3\text{Cl}$ )
  - ✓ Spherical symmetric top molecules ( $\text{CH}_4$ )
  - ✓ Asymmetric top molecules ( $\text{H}_2\text{O}$ ,  $\text{O}_3$ )
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- The structure of a molecule determines whether the molecule has a permanent dipole or may acquire the dipole. The presence of the dipole is required for absorption/emission processes by the molecules.

**NOTE:** Gaseous absorption and emission is discussed in Lectures 6-7

# Atmospheric Aerosols

- Atmospheric aerosols are solid or liquid particles or both suspended in air with diameters between about  $0.002\text{ }\mu\text{m}$  to about  $100\text{ }\mu\text{m}$ .
- **Interaction of the particulate matter (aerosols and clouds particles) with electromagnetic radiation is controlled by particle size, composition and shape.**
- Atmospheric particles vary greatly in sources, production mechanisms, sizes, shapes, chemical composition, amount, distribution in space and time, and how long they survive in the atmosphere (i.e., lifetime).

**Primary and secondary aerosols:**

**Primary atmospheric aerosols** are particulates that emitted directly into the atmosphere (for instance, sea-salt, mineral aerosols (or dust), volcanic dust, smoke and soot, some organics).

**Secondary atmospheric aerosols** are particulates that formed in the atmosphere by gas-to-particles conversion processes (for instance, sulfates, nitrates, some organics).

**Location in the atmosphere:** stratospheric and tropospheric aerosols;

**Geographical location:** marine, continental, rural, industrial, polar, desert aerosols, etc.

**Anthropogenic (man-made) and natural aerosols:**

**Anthropogenic sources:** various (biomass burning, gas to particle conversion; industrial processes; agriculture's activities)

**Natural sources:** various (sea-salt, dust storm, biomass burning, volcanic debris, gas to particle conversion)

**Chemical composition:**

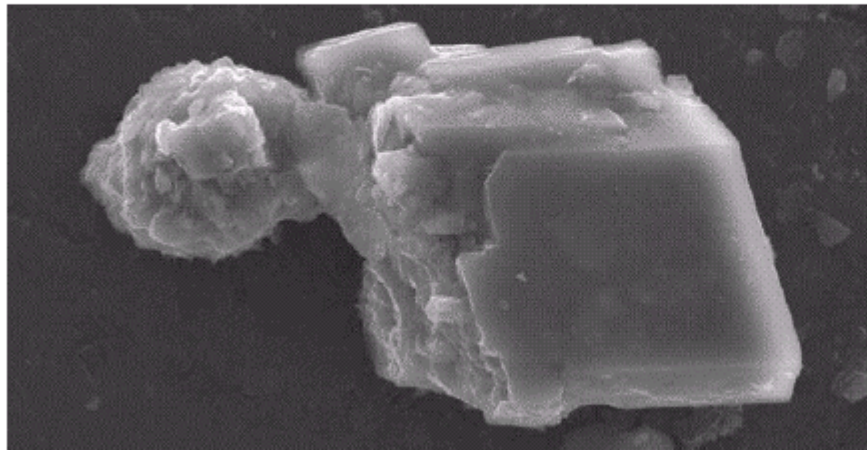
**Individual chemical species:** **sulfate** ( $\text{SO}_4^{2-}$ ), **nitrate** ( $\text{NO}_3^-$ ), **soot** (elemental carbon), **sea-salt** ( $\text{NaCl}$ ); minerals (e.g., quartz,  $\text{SiO}_2$ )

**Multi-component (MC) aerosols:** complex make-up of many chemical species (called internally mixed particles)

**Shape:**

**Spheres:** all aqueous aerosol particles (e.g., sulfates, nitrates, etc.)

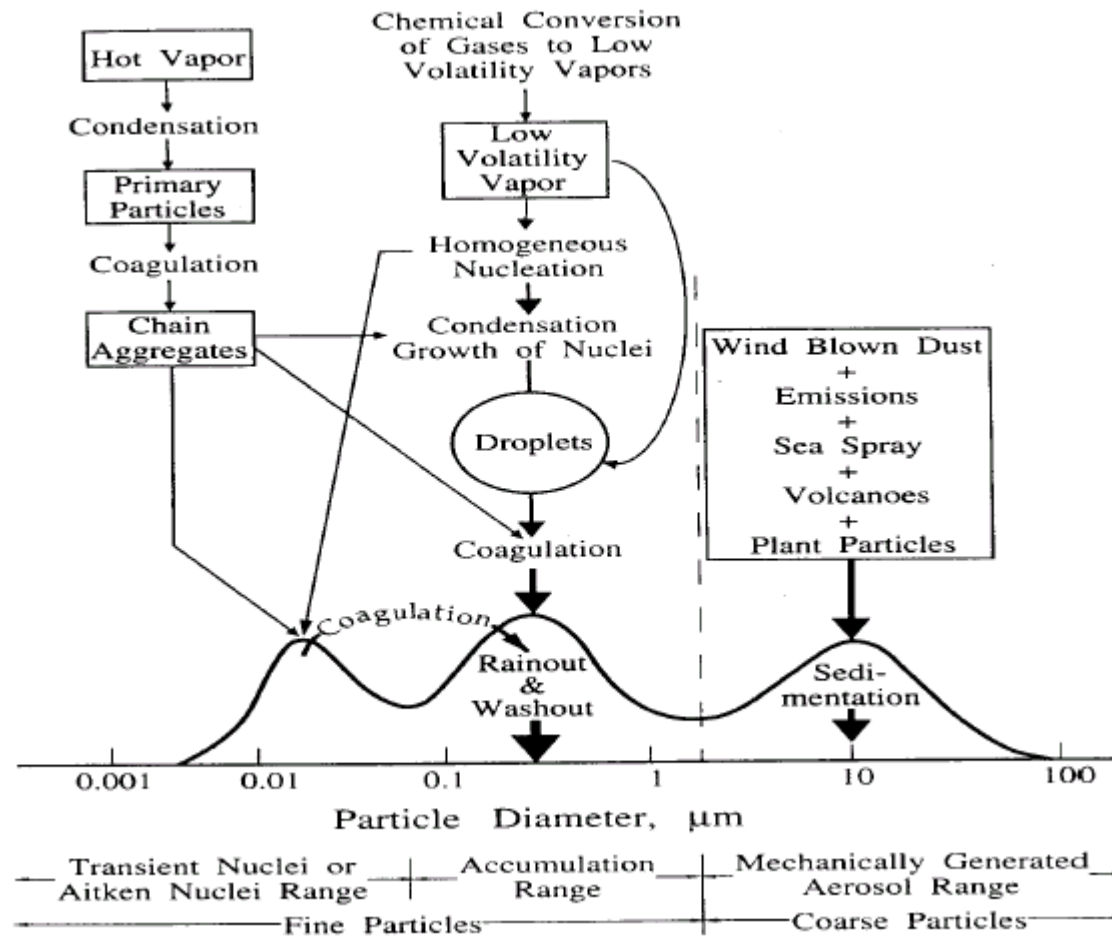
**Complex shapes:** dust, soot (i.e., solid particles)



Scanning electron microscope image of feldspar (mineral dust particle).

**Particle size:**

**Figure 4.2** Idealized schematic of the distribution of particle surface area of an atmospheric aerosols (from Whitby and Cantrell, 1976).



**NOTE: fine mode** ( $d < 2.5 \mu\text{m}$ ) and **coarse mode** ( $d > 2.5 \mu\text{m}$ ); fine mode is divided on the **nuclei mode** (about  $0.005 \mu\text{m} < d < 0.1 \mu\text{m}$ ) and **accumulation mode** ( $0.1 \mu\text{m} < d < 2.5 \mu\text{m}$ ).

- **The particle size distribution** of aerosols are often approximated by a sum of three log-normal functions as

$$N(r) = \sum_i \frac{N_i}{\sqrt{2\pi} \ln(\sigma_i)} \frac{1}{r} \exp\left(-\frac{\ln(r / r_{0,i})^2}{2 \ln(\sigma_i)^2}\right)$$

where  $N(r)$  is the particle number concentration,  $N_i$  is the total particle number concentration of i-th size mode with its median radius  $r_{0,i}$  and geometric standard deviation  $\sigma_i$ .



# Spatial distribution of aerosols

Atmospheric aerosols exhibit complex, heterogeneous distributions, both spatially and temporally.

**Once in the atmosphere, aerosols evolve in time and space:**

- May be transported downwind from the source (by advection, turbulent mixing, etc.);
- May be removed from the atmosphere (by dry deposition, wet removal, and gravitational sedimentation);
- Can change their size and composition due to microphysical transformation processes (such as nucleation, coagulation, and condensation/evaporation);
- Can undergo chemical transformation (via aqueous or heterogeneous chemistry);
- Can undergo cloud processing.

**Figure 4.3** The global distribution of aerosol optical depth as predicted by climate transport models (Tegen et al., 1997).

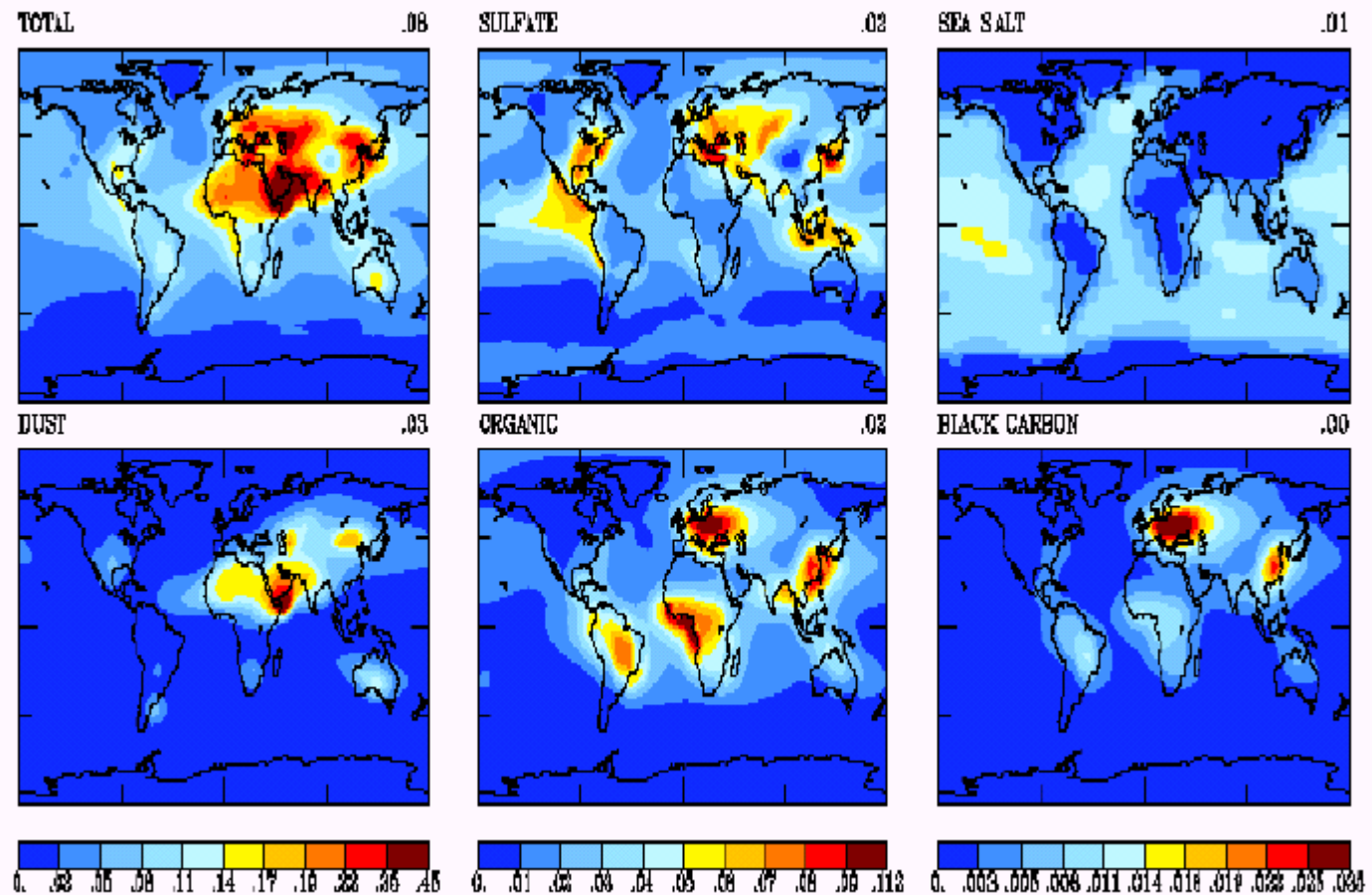


Table 4.3 Global emission estimates for major aerosol types (**estimated flux Tg yr<sup>-1</sup>**)

<i>Source</i>	<i>Low</i>	<i>High</i>	<i>Best</i>
<b>NATURAL</b>			
<b><u>Primary:</u></b>			
soil dust	1000	3000	1500
sea salt	1000	10000	1300
volcanic dust	4	10000	30
biological debris	26	80	50
<b><u>Secondary:</u></b>			
sulfates from biogenic gases	80	150	130
sulfates from volcanic SO <sub>2</sub>	5	60	20
organic matter from biogenic VOC	40	200	60
nitrates	15	50	30
<b><u>Total natural</u></b>	2200	23500	3100

<i>Source</i>	<i>Low</i>	<i>High</i>	<i>Best</i>
<b>ANTHROPOGENIC</b>			
<b><u>Primary:</u></b>			
industrial particulates	40	130	100
dust	300	1000	600
soot	5	20	10
<b><u>Secondary:</u></b>			
sulfates from SO <sub>2</sub>	170	250	190
biomass burning	60	150	90
nitrates from NO <sub>x</sub>	25	65	50
organics from anthropogenic VOC	5	25	10
<b><u>Total anthropogenic</u></b>	600	1640	1050
<b>Total</b>	2800	26780	4150

# Clouds

**Major characteristics are *cloud type, cloud coverage, liquid water content of cloud, cloud droplet concentration, cloud droplet size.***

Important properties of clouds:

- Cloud droplet sizes vary from a few micrometers to 100 micrometers with average diameter in 10 to 20  $\mu\text{m}$  range.
- Cloud droplet concentration varies from about  $10\text{ cm}^{-3}$  to  $1000\text{ cm}^{-3}$  with average droplet concentration of a few hundred  $\text{cm}^{-3}$ .
- The liquid water content of typical clouds, often abbreviated LWC, varies from approximately  $0.05$  to  $3\text{ g(water) m}^{-3}$ , with most of the observed values in the  $0.1$  to  $0.3\text{ g(water) m}^{-3}$  region.

**NOTE:** Clouds cover approximately 60% of the Earth's surface. Average global coverage over the oceans is about 65% and over the land is about 52%.

Table 4.4 Types and properties of clouds.

<i>Type</i>	<i>Height of base (km)</i>	<i>Freq. over oceans (%)</i>	<i>Coverage over oceans (%)</i>	<i>Freq. over land (%)</i>	<i>Coverage over land (%)</i>
<b>Low level:</b>					
<b>Stratocumulus(Sc)</b>	0-2	45	34	27	18
<b>Stratus (St)</b>	0-2	(Sc+St)	(Sc+St)	(Sc+St)	(Sc+St)
<b>Nimbostratus (Ns)</b>	0-4	6	6	6	5
<b>Mid level:</b>					
<b>Altostratus (As)</b>	2-7	46	22	35	21
<b>Altostratus (As)</b>	2-7	(Ac+As)	(Ac+As)	(Ac+As)	(Ac+As)
<b>High level:</b>					
<b>Cirrus (Ci)</b>	7-18	37	13	47	23
<b>Cirrostratus (Cs)</b>	7-18	Ci+Cs+Cc	Ci+Cs+Cc	Ci+Cs+Cc	Ci+Cs+Cc
<b>Cirrocumulus (Cc)</b>	7-18				
<b>Clouds with vertical development</b>					
<b>Cumulus (Cu)</b>	0-3	33	12	14	5
<b>Cumulonimbus (Cb)</b>	0-3	10	6	7	4

- Cloud droplets size distribution is often approximated by a modified gamma distribution

$$N(r) = \frac{N_0}{\Gamma(\alpha)r_n} \left( \frac{r}{r_n} \right)^{\alpha-1} \exp(-r/r_n)$$

where  $N_0$  is the total number of droplets ( $\text{cm}^{-3}$ );  $r_n$  is the radius that characterizes the distribution ;  $\alpha$  is the variance of the distribution, and  $\Gamma$  is the gamma function.

Table 4.5 Characteristics of representative size distributions of some clouds

(for  $\alpha=2$ )

Cloud type	$N_o$ ( $\text{cm}^{-3}$ )	$r_m$ ( $\mu\text{m}$ )	$r_{\max}$ ( $\mu\text{m}$ )	$r_e$ ( $\mu\text{m}$ )	$l$ ( $\text{g m}^{-3}$ )
Stratus:					
over ocean	<b>50</b>	<b>10</b>	<b>15</b>	<b>17</b>	<b>0.1-0.5</b>
over land	<b>300-400</b>	<b>6</b>	<b>15</b>	<b>10</b>	<b>0.1-0.5</b>
Fair weather cumulus	<b>300-400</b>	<b>4</b>	<b>15</b>	<b>6.7</b>	<b>0.3</b>
Maritime cumulus	<b>50</b>	<b>15</b>	<b>20</b>	<b>25</b>	<b>0.5</b>
Cumulonimbus	<b>70</b>	<b>20</b>	<b>100</b>	<b>33</b>	<b>2.5</b>
<b>Altostratus</b>	<b>200-400</b>	<b>5</b>	<b>15</b>	<b>8</b>	<b>0.6</b>

Mean radius:  $r_m = (\alpha + 1) r_n$

Effective radius:  $r_e = (\alpha + 3) r_n$

Cloud liquid water content:

$$l = \rho V = \frac{4}{3} \rho \int \pi r^3 N(r) dr$$

### **Cloud Ice Crystals**

Ice crystals present in clouds found in the atmosphere are often six-sided. However, there are variations in shape:

Plates - nearly flat hexagon

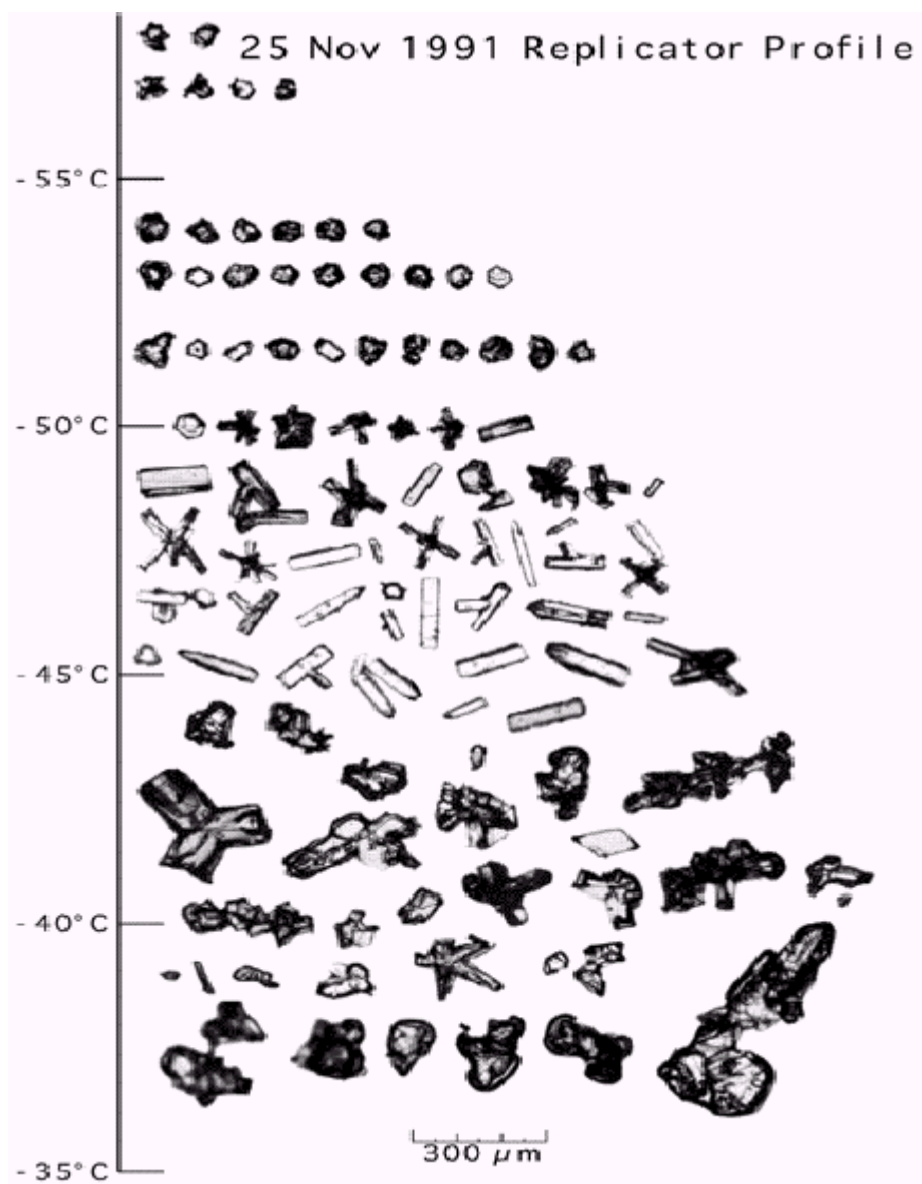
Columns - elongated, flat bottoms

Needles - elongated, pointed bottoms

Dendrites - elongated arms (six), snowflake shape

- Ice crystal shapes depend on temperature and relative humidity. Also, crystal shapes can be changed due to collision and coalescence processes in the clouds.





## 2. Structure of the Atmosphere

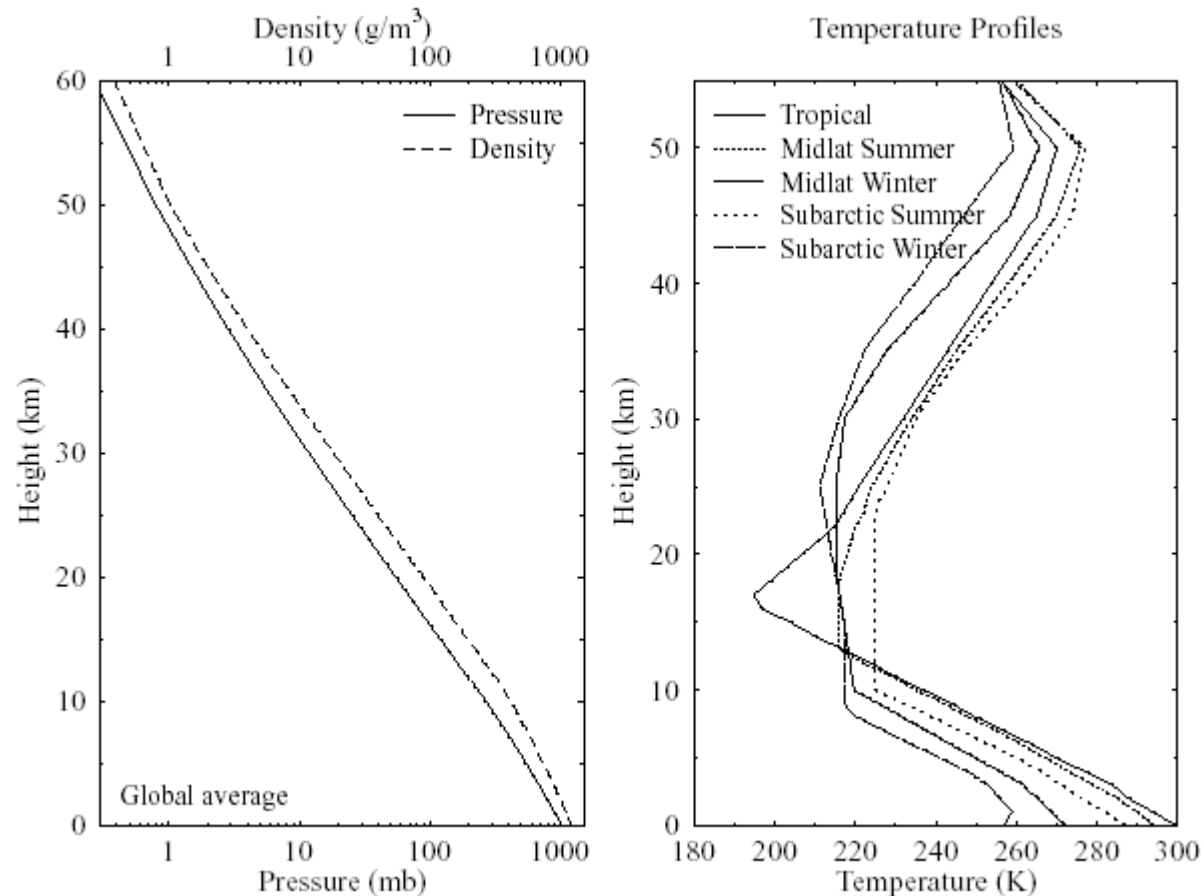
- Variations of temperature, pressure and density are much larger in vertical directions than in horizontal. This strong vertical variations result in the atmosphere being **stratified** in layers that have small horizontal variability compare to the variations in the vertical.

The Earth's atmosphere is divided into four general layers according to the temperature structure:

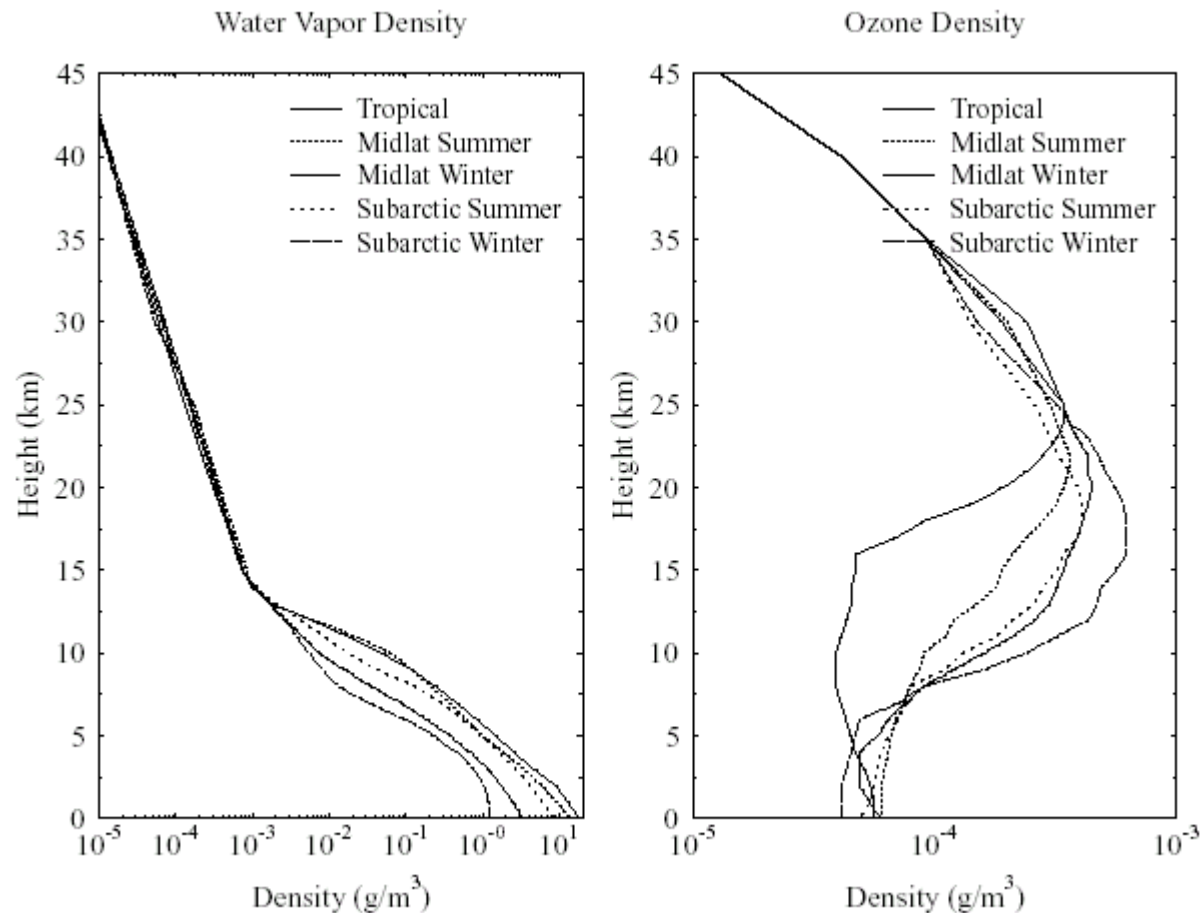
Region	Height range	Temperature trend
Troposphere	0 to 8 to 18 km	decreasing
Stratosphere	to $\approx 50$ km	steady or increasing
Mesosphere	to $\approx 90$ km	decreasing
Thermosphere	above 90 km	increasing

The temperature increases with height in Earth's stratosphere due to absorption of solar UV radiation by ozone. Venus and Mars do not have a stratosphere and mesosphere because they lack ozone (from oxygen).

**Figure 4.4** Temperature profiles of the standard atmospheric models often used in radiative transfer calculations. “Standard U.S. 1976 atmosphere” is representative of the global mean atmospheric conditions; “Tropical atmosphere” is for latitudes  $< 30^\circ$ ; “Subtropical atmosphere” is for latitudes between  $30^\circ$  and  $45^\circ$ ; “Subarctic atmosphere” is for latitudes between  $45^\circ$  and  $60^\circ$ ; and “Arctic atmosphere” is for latitudes  $> 60^\circ$ .



Water vapor and ozone density profiles of standard Earth atmospheres.



The water vapor density is mainly a function of temperature in the troposphere due to the strong dependence of the saturation vapor density on temperature. Water vapor is a trace gas in the stratosphere.

The ozone amount is lowest in the tropics and highest in the subarctic winter due to the Brewer-Dobson circulation transport from equator to pole.

# Temperature lapse rate

- Except cases with temperature inversion, temperature always decreases in the lower troposphere.

**Temperature lapse rate** is the rate at which temperature decreases with increasing altitude.

$$\Gamma = - (T_2 - T_1) / (z_2 - z_1) = - \Delta T / \Delta z$$

where T is temperature and the height z.

- Adiabatic process is of special significance in the atmosphere because many of the temperature changes that take place in the atmosphere can be approximated as adiabatic.

For a parcel of dry air under adiabatic conditions it can be shown that

$$dT/dz = - g/c_p$$

where  $c_p$  is the heat capacity at constant pressure per unit mass of air and  $c_p = c_v + R/m_a$  and  $m_a$  is the molecular weight of dry air. The quantities  $g/c_p$  is a constant for dry air equal to **9.76 C per km**. This constant is called **dry adiabatic lapse rate**.

- **The law of hydrostatic balance** states, that the pressure at any height in the atmosphere is equal to the total weight of the gas above that level.

**The hydrostatic equation:**  $dP(z) / dz = - \rho(z) g$

where  $\rho(z)$  is the mass density of air at height  $z$ , and  $g = 9.81 \text{ m/s}^2$  is the acceleration of gravity.

- Integrating the hydrostatic equation at constant temperature as a function of  $z$  gives

$$P = P_0 \exp(-z / H)$$

where  $H$  is **the scale height:**  $H = k_B T / mg$ ; and  $m$  is the average mass of air molecule ( $m = 4.8096 \times 10^{-26} \text{ kg/air molecule}$ ).

# Air motion

*The key energy sources driving the wind systems on our planet:*

- a) **Solar radiation** (energy emitted by Sun)
- b) Latent heat
- c) **Thermal radiation** (energy emitted by the surface of the Earth and the atmosphere)

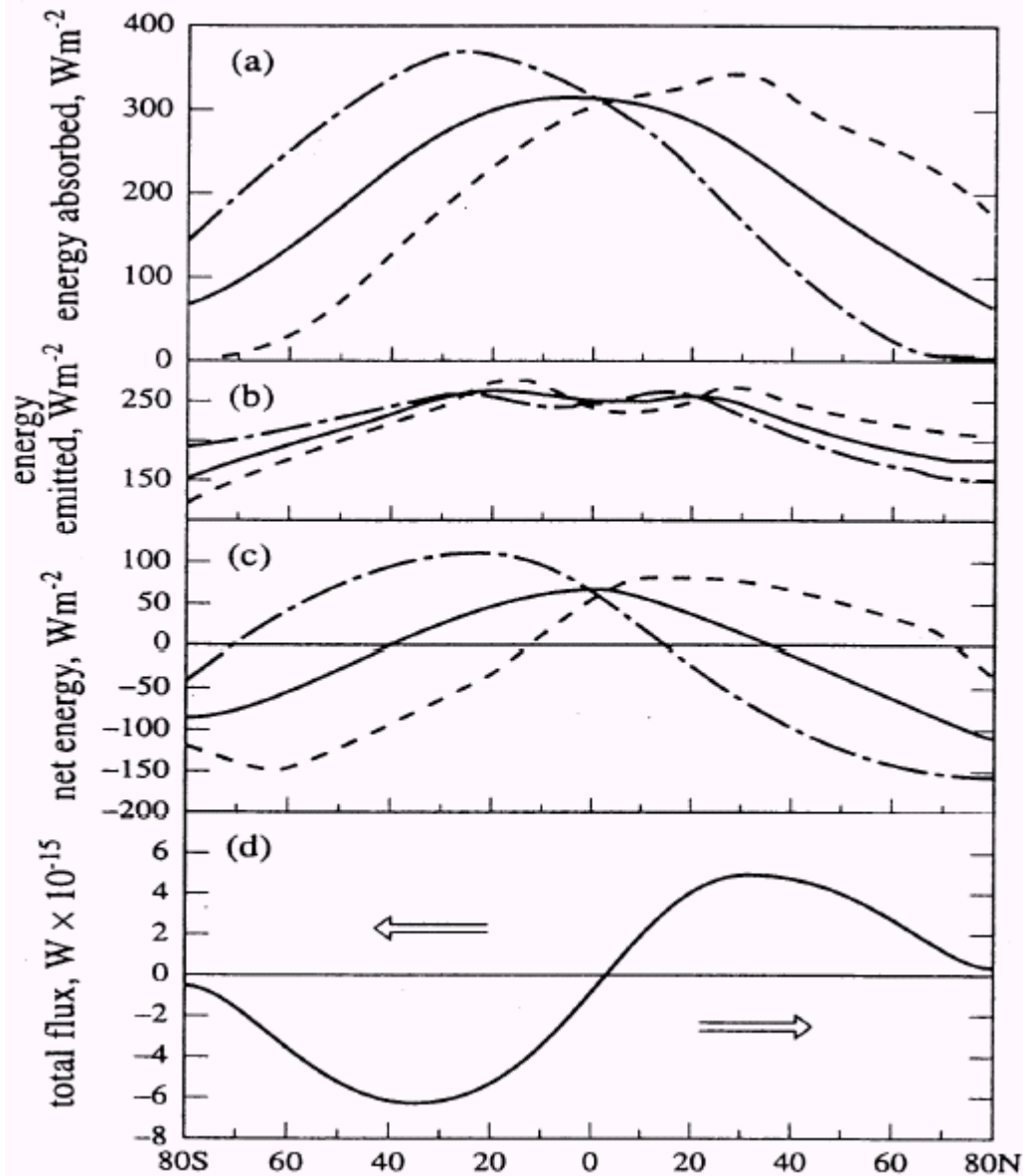


Figure 4.5. Latitudinal distribution of radiative fluxes at TOA, except (d) which gives the horizontal flux that must be carried across latitudes. Solid curves are annual averages, dash-dot and dashed curves are averages over NH winter and summer months respectively (from Goody, 1995).



**NOTE:**

- The uneven distribution of solar energy results from latitudinal variations in solar insolation (more in tropics, less at poles), and from differences in absorptivity of the Earth's surface. It creates the large-scale air motion to transport energy from the tropics toward the polar regions.
- This energy transport is affected by the rotation of Earth (the Coriolis effect). Thus, the general pattern of global air circulation is chiefly due to both solar radiation and Earth rotation.

Figure 4.6 Global energy budget.

